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**JOHN F. KENNEDY SPACE CENTER
UNIVERSITY OF CENTRAL FLORIDA**

**DEVELOPMENT OF AN ACCELERATED TEST METHOD FOR THE DETERMINATION
OF SUSCEPTIBILITY TO ATMOSPHERIC CORROSION**

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ABSTRACT

The theoretical rationale is presented for utilization of a repetitive cyclic current reversal voltammetric technique for characterization of localized corrosion processes, including atmospheric corrosion. Applicability of this proposed experimental protocol is applied to characterization of susceptibility to crevice and pitting corrosion, atmospheric corrosion and stress corrosion cracking. Criteria upon which relative susceptibility is based have been determined and tested using two iron-based alloys commonly in use at NASA/KSC - A36, a low carbon steel and 4130, a low alloy steel.

Practicality of the procedure has been demonstrated by measuring changes in anodic polarization behavior during high frequency current reversal cycles of 25 cycles per second with 1 mA/cm^2 current density amplitude in solutions containing Cl^- . The results demonstrated that, due to excessive polarization which affects conductivity of barrier corrosion product layers, A36 was less resistant to atmospheric corrosion than its 4130 counterpart - behavior which has also been demonstrated during exposure tests.

SUMMARY

Based on an analysis of factors which are known to contribute to the overall corrosion process, galvanostatic electrochemical procedures show greater promise for creating an environment during accelerated testing which more closely simulates natural environments than do conventional potentiostatic methods. Similarly, since both anodic and cathodic reactions occur simultaneously on the surfaces of freely corroding metals, it is necessary to periodically reverse the direction of current flow. On the basis of these modelling simulation requirements, the Repetitive Current Reversal Voltammetry technique has been developed.

Using a galvanostat to supply current, and a storage oscilloscope to measure potential transients as a function of time, a methodology and associated predictive criteria have been generated using two representative alloys found in common use at NASA/KSC - A36 steel and 4130 low alloy steel. By trial and error, the optimum combination of impressed current amplitude and current reversal cycle frequency has been found which will differentiate environmental degradation behavior for these two metals - +/- 2 milliamperes current amplitude with a 25 cycles per second current reversal frequency.

Results to date suggest that susceptibility to various localized corrosion forms of attack may be associated with "over-polarization", that is, too high an electrical resistivity for insoluble corrosion product barrier layers which form at the metal/environment interface. In the presence of aggressive ions such as the chloride ion, these high potential drops or fields across the barrier layers "draws" these aggressive anions into the film, causes its decrease in resistivity and eventually leads to the inability of passivity being maintained.

This report summarizes many of the insights, opinions and perspectives of the author which may prove useful to others as they contemplate developing experimental procedures for the study of environmental degradation of materials.

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1.0 INTRODUCTION

The vast majority of electrochemical test methods used in corrosion science experimentation derive from potentiostatic polarization techniques - i.e. a measurement of current required to maintain the potential of a metal at some reference value. As the name implies, the electronic instrumentation fixes potential by regulation of current. As a consequence of this functionality, corrosion rates [current] vary with time as the externally maintained potential remains fixed [potentiostatic] or is varied [potentiodynamic sweep] during the course of the experiment.

A number of "accelerated" corrosion test procedures are based upon potentiostatic polarization procedures - linear current versus applied potential relationships or "polarization curves", low amplitude linear polarization for determination of "polarization resistance", low amplitude cyclic polarization or "AC impedance" and linear cyclic voltammetry or "LCV" to name but a few. Although a great deal of information has been obtained through such experimentation, some of it even useful, attempts to correlate long term corrosion behavior with the results of such procedures have often been fraught with inconsistencies, irreproducibilities and difficulties with interpretation. The problem, as I see it, is that the basis for these techniques - potential or polarization control - is not a suitable or accurate model for the way metals behave in "real life" situations. The true basis is, in fact, just the opposite.

When a metallic material is exposed to a corrosive environment, there develops, rather quickly, an electrochemical potential across the metal/environment interface which serves to drive those chemical reactions which contribute to that particular electrochemical potential. Corrosion processes consist of one or more anodic or oxidation reactions which, in a physical sense, carry current out from the surface of the metal and into the environment. Anodic current is balanced by a cathodic current of equal amplitude which flows into the metal from the environment, carried by one or more reduction reactions. The respective current flows produce, due to a electrical resistance which opposes the flow of current [polarization resistance], a shift in potential or polarization equal to the product of the current flow and the resistance through which that current flows. The resulting so-called "mixed" or corrosion potential of the material is positioned between the reversible potentials for the various electrochemical processes, the displacement being dependent upon the polarization resistance for the various contributing electrochemical reactions. Mathematical models of electrochemical kinetics [e.g. Butler-Volmer equation] have been used to characterize the relationship between current and applied potential, resulting in what have come to be known as "Evans Diagrams". A schematic representation of current flow across the metal/environment interface is shown in Figure 1.

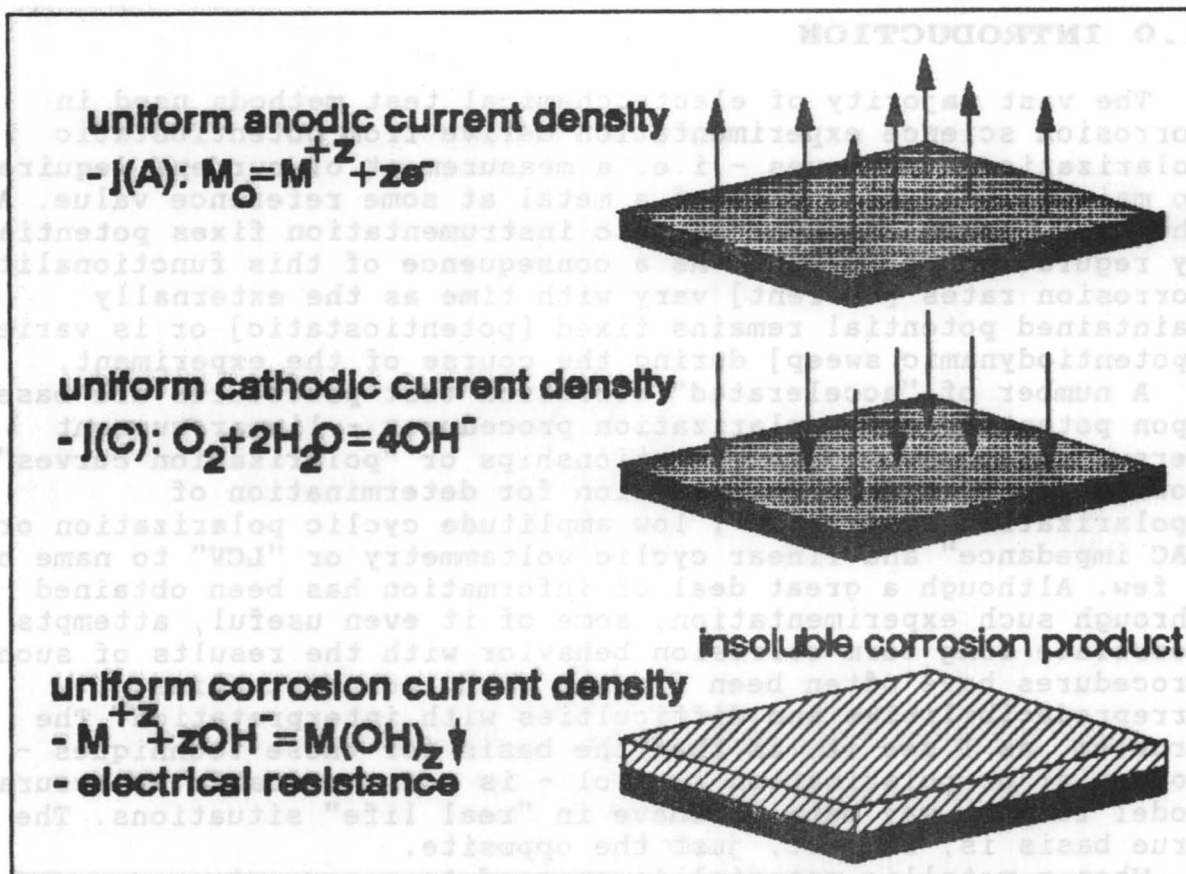


Figure 1 - Schematic showing physical sense of current direction - anodic current leaving metal and cathodic current entering it.

The point to be made is simply this: Since the corrosion potential of the material is determined by polarization, specifically polarizability of the material as influenced by the contributing electrochemical reactions, then it is the flow of current which controls potential, not the other way around. Fixing or controlling the potential of the material will cause current flow to conform to the degree of polarization - if there is any change in resistance to current flow which occurs as a natural consequence of the chemical reactions taking place during service exposure, then current will change accordingly. One such occurrence, the evolution of insoluble reaction products which block the flow of current across the interface, is also shown in Figure 1. Under "natural", free corroding conditions, it would seem that development of insoluble corrosion products with whatever inherent intrinsic electrical and ionic transport resistivity they possess would cause the corrosion potential to shift in one direction or another with respect to a film-free metal/electrolyte interface. Since many metal oxides and hydroxides [iron based, e.g.] provide greater resistance to the anodic current flow [ion transport control], the corrosion

potential under natural conditions tends to shift toward more positive values. When experimental simulation of corrosion processes are under potentiostatic control, the potential, of course, is fixed. There are two consequences of this control. One, the corrosion current would not be expected to be the same as under natural control conditions, resulting in lack of correspondence with long term corrosion rates. Secondly, since the potential of the metal determines what electrochemical reactions can occur, differences in potential may result in altogether different reaction products being generated. Since it is the reactions products which determine the nature of insoluble reaction products, and it is the insoluble reaction products which affect both degree of polarization and amplitude of the corrosion current, the end result is most likely a continual divergence of experimental corrosion rates from the real ones.

A second negative characteristic associated with potentiostatic control of electrochemical processes derives from the configuration of the system used to control the process being studied. Under anodic polarization - when the potential of the material is driven to higher [more positive] values than its corrosion or steady-state value - the current which produces this polarization leaves the material [working electrode], flows through the electrolyte and enters a remote auxiliary [counter] electrode. In a freely corroding metal, on the other hand, current leaves and enters the same exposed surface, albeit not necessarily at the same point on that surface. What this means is that cathodic and anodic reactions do not occur concurrently on the same metal surface - more significantly, the reaction products of these electrochemical processes are not produced at a common surface. Since most insoluble corrosion products which form in aqueous environments contain metal cations, hydroxide ions and other constituent anions [SO_4^{2-} , Cl^- , CO_3^{2-} , etc.], isolating anode from cathode in the electrochemical cell changes the localized chemistry associated with the natural or free corrosion process [Figure 2].

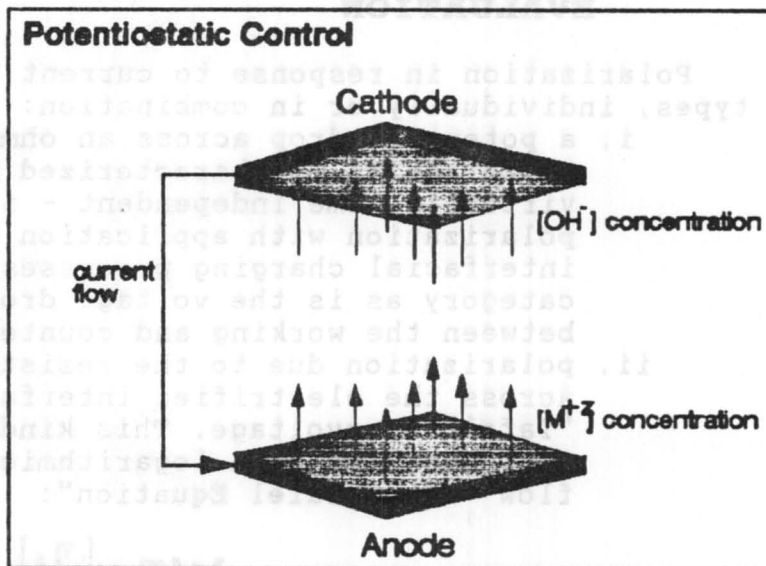


Figure 2 - Schematic representation of the separation of anode and cathode in an electrochemical cell utilizing potentiostatic control.

1.1 THEORETICAL BASIS for PROPOSED EXPERIMENTAL PROCEDURE

Measurement of degree of polarization which result from impressed current is not a new technique, having been used for some time as an analytical chemistry technique - chronopotentiometry, stripping voltammetry, etc. It has not been used to any great extent in corrosion science applications. It would seem, however, to be most appropriate in measuring the behavior of a material in response to flow of current across the metal/environment interface. By impressing a constant [galvanostatic] current between an inert electrode [platinum counter] and the material being characterized [working electrode], the potential change or polarization can be measured as a function both of time and of the amplitude of the impressed current. In order to simulate "natural" conditions, the current direction should be regularly reversed in order to develop concentrations of both kinds of reaction products at the metal interface - anodic and cathodic. Thus evolves the name of the technique - "CYCLIC CURRENT REVERSAL VOLTAMMETRY". The experimental variable to be measured will be the rate of change in material potential, or "polarization rate".

1.1.1 CRITERIA for CORROSION SUSCEPTIBILITY EVALUATION

Polarization in response to current flow can be of three types, individually or in combination:

- i. a potential drop across an ohmic resistance. This polarization is characterized by a $V=IR$ response, and is virtually time independent - i.e. instantaneous polarization with application of current. Capacitance or interfacial charging processes are included in this category as is the voltage drop across the electrolyte between the working and counter electrodes.
- ii. polarization due to the resistance to charge transfer across the electrified interface - i.e. so-called "Tafel" overvoltage. This kind of polarization is characterized by a logarithmic dependence upon current flow - the "Tafel Equation":

$$\ln[I] = -\left[\frac{\eta_a}{\beta_a}\right]$$

where n_1 = degree of polarization produced by current I
and β_1 = charge transfer resistance.

- iii. the potential drop across an insoluble reaction product or film which forms at the metal/electrolyte interface. The degree of polarization is a function of the resistivity of the reaction product, the polarization rate is a function of the nucleation/growth kinetics of the deposition process. It is this polarization process with which we will be most interested.

A schematic representation of the polarization extremes - polarization resistance during active metal dissolution versus IR resistance across an insoluble corrosion product - is shown in Figure 3.

Under conditions of repetitive current reversal, any change in either degree or in rate of polarization signifies changes in the one of the three processes enumerated above. Of the three, only the third should provide any significant contribution. Thus, by evaluating such changes, we should be able to establish criteria for evaluating the environmental stability of a particular material in a given environment.

As "protective" films grow on bare or air-formed film covered

metal substrates, there should be a regular increase in degree of polarization with each consecutive anodic cycle. Furthermore, the degree of polarization should progressively decrease as well, if the protective film is becoming more and more protective. Any change in this trend will be interpreted as an indication of development of instability in the system - a loss in ability of the system to resist the corrosive actions of the environment.

1.1.2 EXAMPLES OF HOW CRITERIA ARE APPLIED

NASA/KSC is interested in predictive capability with respect to a large number of environmental degradation of materials problems. Specifically, accelerated test methods for predicting long term resistance of coated and uncoated metals to atmospheric

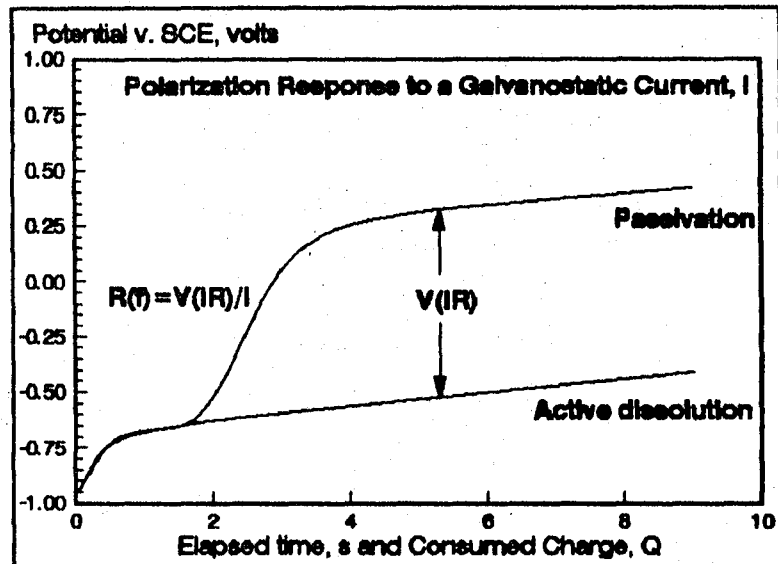


Figure 3 - Schematic representation of limiting cases in polarization behavior - metal dissolution v. insoluble corrosion product.

corrosion are needed for rapid, early screening of candidate materials. Susceptibility to crevice corrosion, pitting and stress corrosion cracking - all localized forms of corrosion attack - is another area to which this approach can be applied in developing accelerated test methodology.

1.1.2.1 ATMOSPHERIC CORROSION

Atmospheric corrosion can occur in two forms - at elevated temperatures by direct reaction between material and corrosive gasses, and through electrochemical means by interaction between material and condensed aqueous liquid films. KSC is considered one of the most, if not the most, severe locations for atmospheric corrosion in the world. This is due to its proximity to the ocean and to the corrosive nature of combustion products from Space Shuttle solid fuel rocket boosters [SRBs].

During atmospheric corrosion under condensed moisture films, the actual corrosion process naturally takes place only when the film is present upon the surface - long term exposure testing as, for instance, is performed at NASA-KSC's seaside test site, provides an integrated measure of atmospheric corrosion behavior under those conditions where condensation is present. Ocean spray, rain, condensation of dew, etc. provide the natural environment. The process of condensation and evaporation actually increases the severity of the attack over what it would be under constant exposure conditions - and, as such, provides a clue as to an appropriate acceleration procedure.

As Figure 4 demonstrates, although initial, as-condensed electrolyte concentrations may fall below a critical level to initiate corrosive attack [$<5 \times 10^{-3} \text{ M Cl}^{-1}$ for carbon steels, e.g.], a critical level can be achieved during evaporation. During test site exposures, this condition is only reached during some fraction of the total exposure times. Rainwater and dew condensation tend to return the process back to square one.

It is therefore proposed that one possible acceleration test would be to increase chloride [or any other aggressive species] by aliquot additions to a stock solution while the metal undergoes repetitive current reversal voltammetry. The time or number of cycles to a point where polarization behavior is affected would be a criteria for comparison of material susceptibility.

Assume some critical [minimum] concentration of chemical species X causes resistivity of film to decrease.

If $C(X)$ in environment is $0.5C^*$, no problem, but..

If $C(X)$ increased, or

If solvent is evaporated, we have a problem - film begins to thin

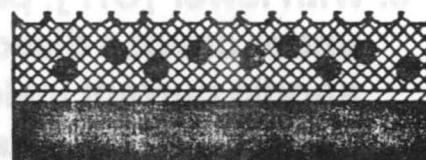
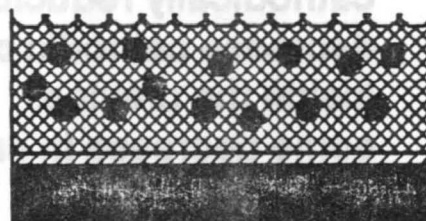
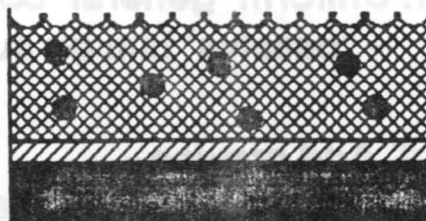


Figure 4 - Schematic representation of how increased solute concentrations can be used to simulate evaporation of condensed moisture layers.

1.1.2.2 CREVICE CORROSION

Metals with the capacity to passivate themselves with barrier surface films [aluminum, stainless steels, nickel and titanium alloys] require a finite hydroxide ion concentration [from the cathodic reduction of oxygen] to retain their passivity. Occluding any area of a passive metal surface - with a crevice, for example, restricts oxygen transport to the creviced area, and leads to breakdown of passivity and active corrosion [Figure 5]. Degree of susceptibility of a material to this form of localized corrosion might also be rapidly characterized by an accelerated test combining Repetitive Current Reversal Voltammetry [RCRV] with oxygen depletion from the electrolyte.

It is proposed that an accelerated method for determination of susceptibility to crevice corrosion would involve the effect of oxygen depletion on RCRV while deaerating the electrolyte.

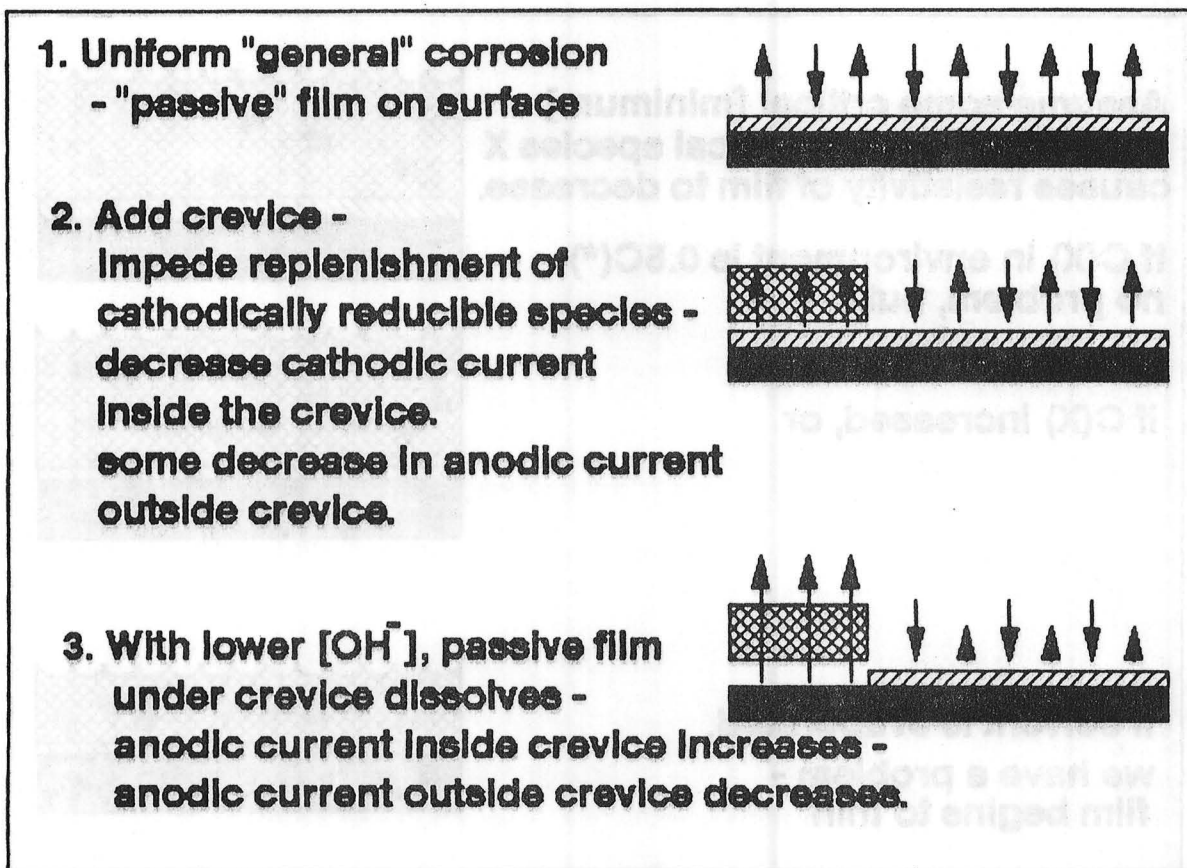


Figure 5 - Schematic representation of how a crevice leads to localized breakdown of passivity.

1.2 PROPOSED EXPERIMENTAL PROTOCOL

- Reversal frequency and current amplitude experimental operational variables.
- Determination of the effect of oxygen depletion on RCRV kinetics.
- Determination of the effect of increased chloride ion concentration on RCRV kinetics.
- Comparison of RCRV kinetics for two different materials for the purposes of distinguishing behavior - procedural feasibility determination.
- Determination of effects of other atmospheric contaminants on RCRV kinetics.
- Development of a "standard" test medium composition and methodology for characterization of atmospheric corrosion resistance.

2.0 EXPERIMENTAL - MATERIALS and EQUIPMENT

Feasibility studies were performed using two relatively common ferrous-based alloys in use at NASA/KSC - A36 [basically a carbon steel] and 4130 [a low alloy steel]. Their compositions are given in Table I.

Based upon these compositions, the A36 alloy would be expected to show the lesser degree of resistance toward atmospheric corrosion attack.

Specimens of the two materials were machined into rectangular configurations, then assembled into the electrode configuration shown in Figure 6. This particular assembly configuration was

selected for a number of reasons - immersion of the tip end of the assembly beneath the electrolyte precludes the need for isolation coating and their inherent tendency of providing crevices for crevice corrosion attack; multiple material

Table I - Elemental Compositions of Iron Alloys Selected for this Study.

A36: 0.29 C(max), 0.8-1.20 Mn,
0.20Cu

4130: 0.28-0.33 C, 0.40-0.60 Mn,
0.15-0.30 Si, 0.8-1.10 Cr,
0.15-.25 Mo

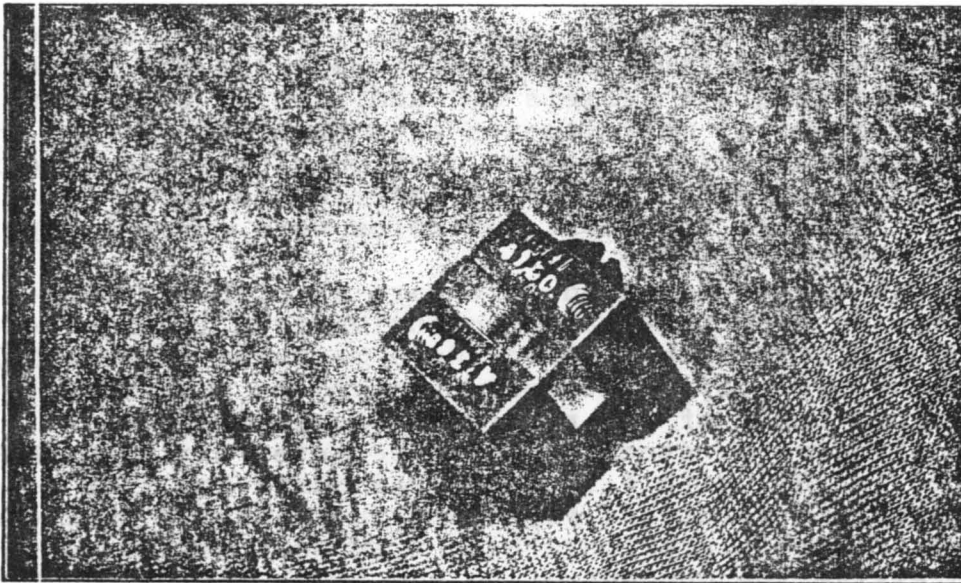


Figure 6 - Photograph of machined samples assembled into the bi-specimen electrode configuration.

experimental runs can be made consecutively in the same

electrolyte without concern for changing, cleaning and repositioning electrodes between experiments.

The electrochemical cell used in these studies was designed and constructed prior to my arrival at KSC - it is shown in Figure 7. It features, in addition to conventional items

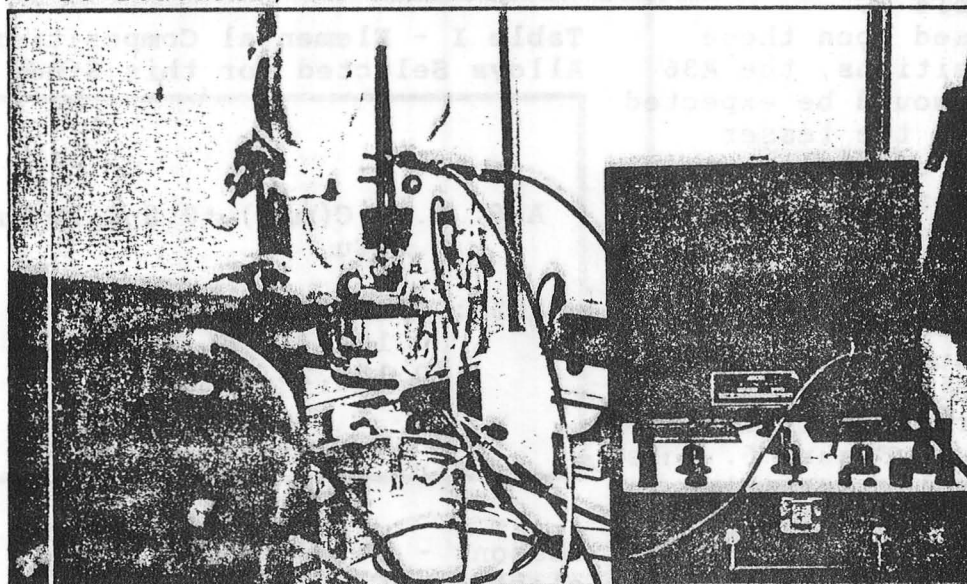


Figure 7 - Photograph of Electrochemical Cell used in these studies.

[reference electrode well/luggin capillary, isolated counter electrode well, working electrode access and gas dispersion tube input], two separate vessels for addition of test solutions.

Electrochemical measurements were obtained using a Tacussel BiPad potentiostat/galvanostat coupled with a signal generator. The waveform selected for these experiments was a square wave function in which the input variables were current amplitude and cycle frequency [Figure 8].

Current amplitudes used here were as high as ± 2 milliamperes with reversal frequencies from 10 milliseconds to 10 seconds. Polarization kinetics were measured using a Tektronics storage oscilloscope. Data was obtained by analysis of photographs taken of the retained screen image.

The standard or stock solution selected was $0.1M\text{ KH}_2\text{PO}_4$ adjusted to $\text{pH}=7$ with $0.1M\text{ NaOH}$. The basis for this selection was that phosphate solutions represent an innocuous environment insofar as steels are concerned. $0.1M\text{ NaCl}$ was added when effect of aggressive ion concentration was to be evaluated. Unless otherwise noted, all solutions used were air-saturated and stagnant.

Prior to running any experiment, specimens were mechanically polished using 100 grit silicon carbide paper, rinsed with distilled water, then dried with absolute ethanol rinse and a blast of warm air before assembling the electrode and placing the

assembly in the electrochemical cell. Solution was added from one of the reservoirs to a level just above the bottom of the electrode assembly. Rest or corrosion potentials were recorded once they had reached some steady state value.

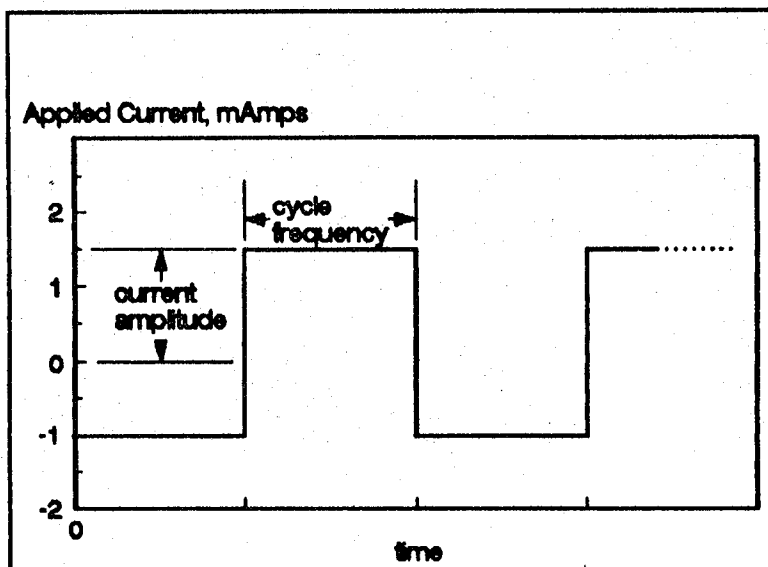


Figure 8 - Schematic of Experimental Procedure with respect to the RCRV control variables.

3.0 EXPERIMENTAL RESULTS and DISCUSSION

In Figure 9, for those who derive comfort from conventional polarization curves, appears a pair of polarization curves describing potentiostatic polarization behavior for A36 steel in air-saturated and deaerated [with N_2] KH_2PO_4 solution [pH 7]. The only feature of interest is the graphic demonstration of the ability of the A36 alloy to passivate in this solution, whether O_2 is present or not. Notice that the potentiostatic method requires a critical anodic current of better than 500 mA to achieve passivation at potentials around -600 mV v SCE. Also note that the critical current requirements are higher in the

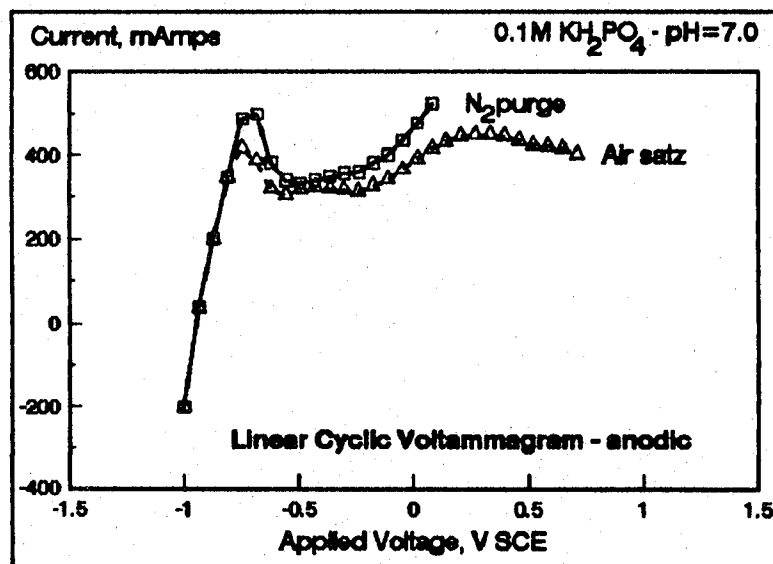


Figure 9 - Conventional Polarization Plot [I v. V] showing the Effects of Oxygen Depletion on Corrosion Kinetics of A36 Alloy.

deaerated solution.

When the same experiment is performed using the low frequency RCRV method, with a ± 10 second frequency and a ± 1.25 mA current amplitude, passivation is produced by the 5th cycle with one four hundredth [1/400] of the anodic current required for the potentiostatic polarization method [Figure 10].

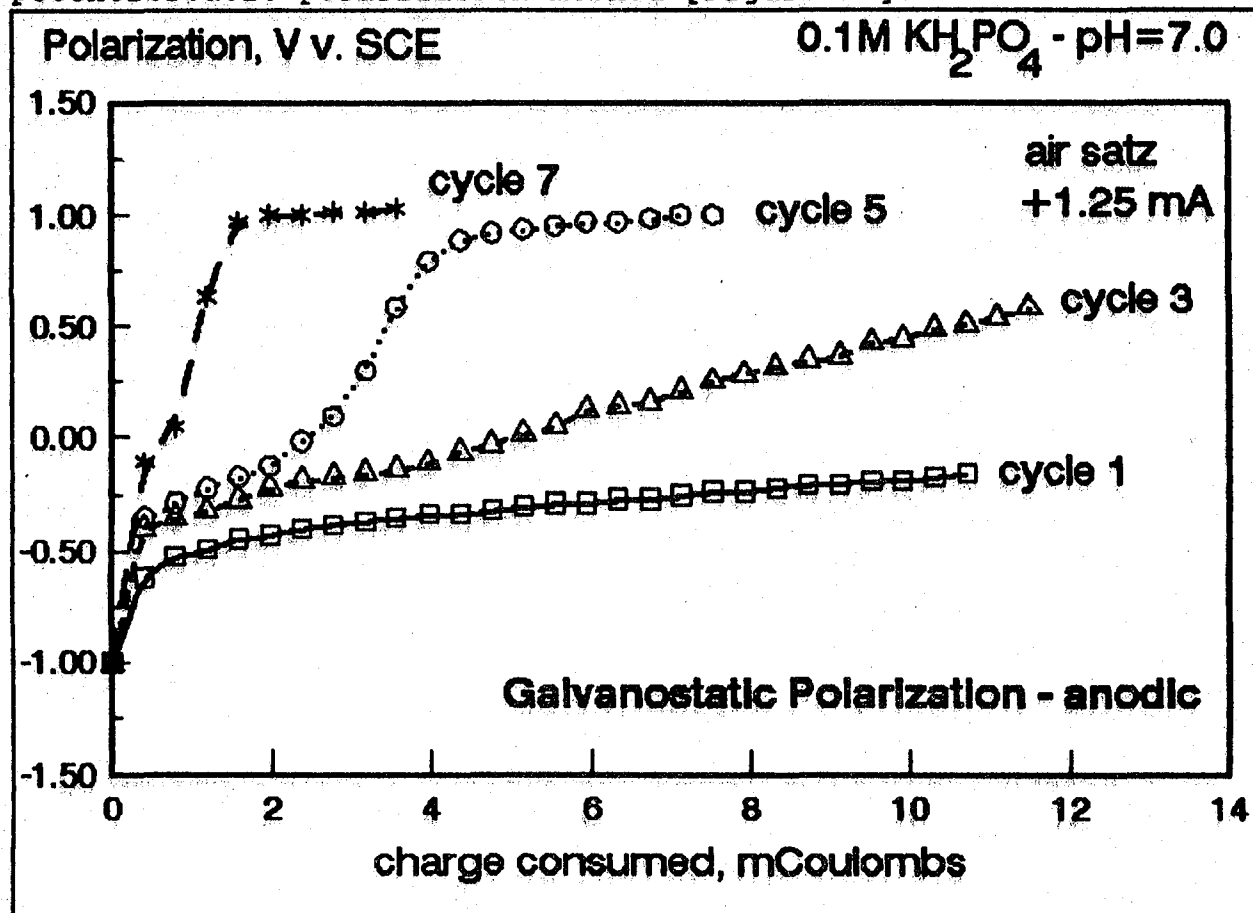


Figure 10 - RCRV plot for A36 alloy in air-saturated stock solution.

These results, as contained within Figures 9 and 10, serve to endorse my argument criticizing the reliance on potentiostatic polarization procedures for prediction of corrosion behavior. Their use, particularly in determining, from Tafel slope measurements, corrosion current densities are misleading to say the least.

RCRV measurements of the 4130 alloy in the stock solution using low frequency current reversals were similar to the results displayed in Figure 10, only the number of cycles to produce passivity were noticeably less - by the 2nd cycle. However, experimental results for both alloys in this stock solution were extremely irreproducible. The problem lies with the electrochemical history of the process. Length of time at open

circuit was of prime consideration - after passivation was achieved with either alloy, it became impossible to distinguish behavior between the two alloys. Specimen pretreatment prior to the experiments was also an influencing factor - surface preparation and finish would affect the results.

Addition of solutions containing chloride ion resulted in inability of both alloys to achieve passivation - the film resistance appeared, however, slightly greater for the 4130 alloy than for the A36. These results also were difficult to reproduce. The point is, unless a definitive criteria can be developed which is independent of operator procedure, the technique will never be applicable as a standard test method.

One problem with the electrochemical cell was that, with its present design, aliquots of solutions containing the aggressive species could not be rapidly mixed with the stock solution. This suggests a design change such that second solution aliquots be added through the gas dispersion valve circuit - in this way, solutions can be rapidly mixed during RCRV sequences.

3.1 HIGH FREQUENCY CURRENT REVERSAL CYCLING

Increasing the cycle frequency increases the stability of the system - at least with respect to reproducibility in measurement. In Figure 11 is plotted polarization kinetics for a single typical cycle when a

± 10 mA amplitude current is impressed for 10 mS cycles. A number of relevant observations are worth noting - When forward and reverse current amplitudes are equal [current balanced], the median potential read from a slow response high impedance voltmeter is remarkably constant. So constant, in fact, this procedure might be considered as a standard test method for measurement of corrosion potentials. Changes in current amplitude results in a shift in median potential to higher or lower values, respectively.

When current amplitudes are unbalanced, the median potential shifts in the direction of the current imbalance. This procedure should also be studied further in that the rate of polarization

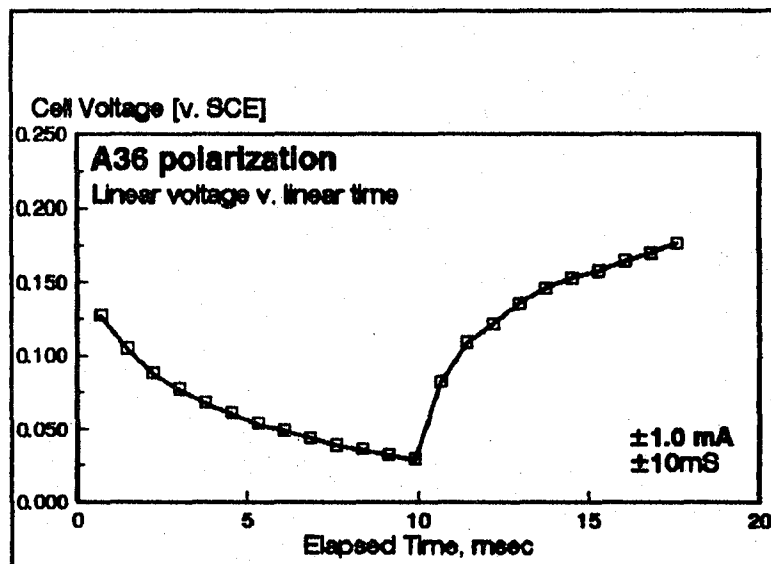


Figure 11 - Polarization kinetics for A36 alloy in the stock solution; experimental parameters shown on graph.

shift appears to reflect the degree of control of the contributing anodic and cathodic electrochemical kinetics on the overall corrosion process.

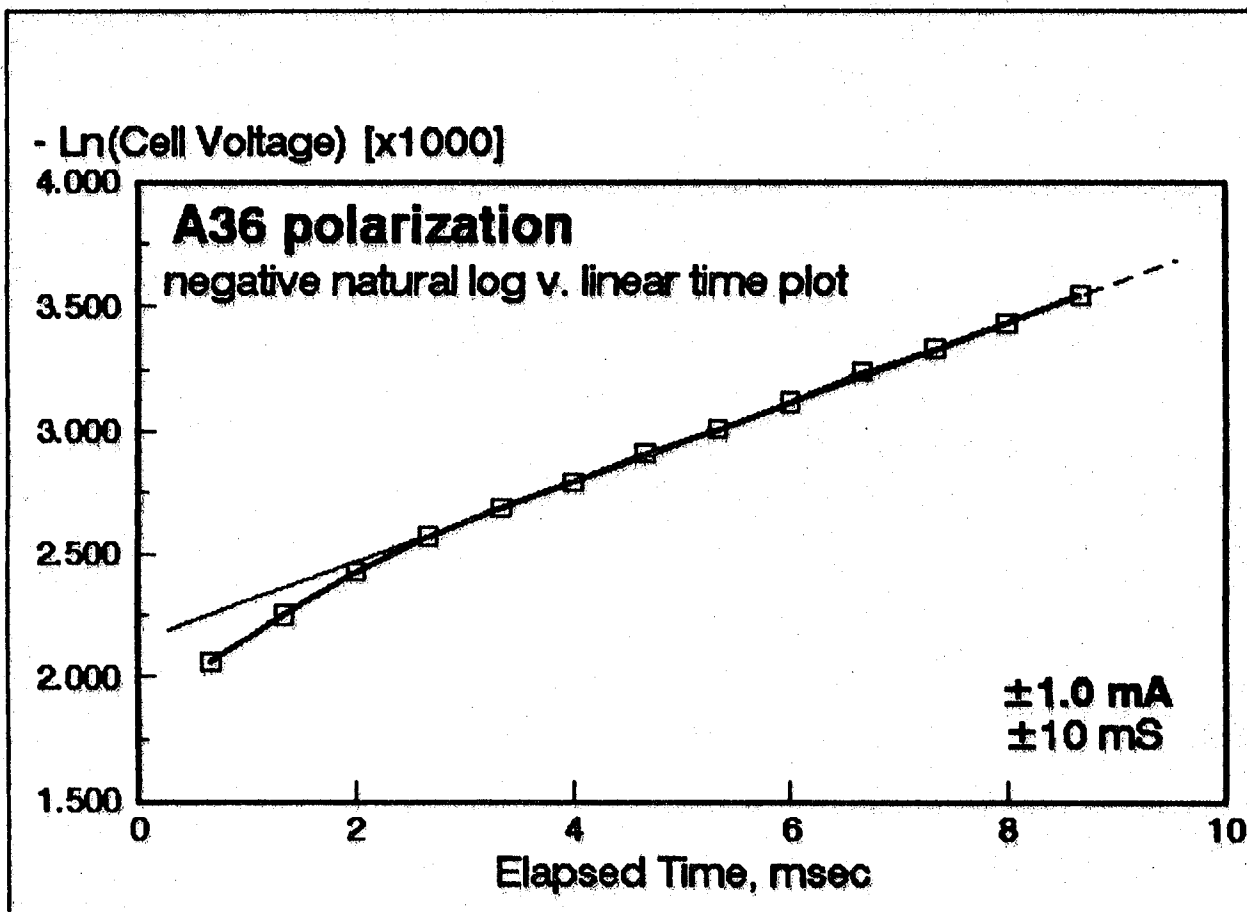


Figure 12 - Replot of Figure 11, plotting $-\ln(\text{volts})$ v. time.

Replotting the data of Figure 11 using the negative natural logarithm of the cell voltage, produces the graph shown in Figure 12. Only the anodic polarization portion of the overall cycle is shown. Although the plot is not a linear function of the plotting variables over the whole range, it fits the later portion of the cycle quite well. Neither an exponential or parabolic plot would do as well. Without drawing any conclusions as to the mechanistic implications to be derived from this, experimental results will be presented in this format, since it is easier to see variations when comparing different alloys and when chloride ion solutions are introduced into the stock solution.

3.2.1 POLARIZATION BEHAVIOR IN 0.1M KH_2PO_4

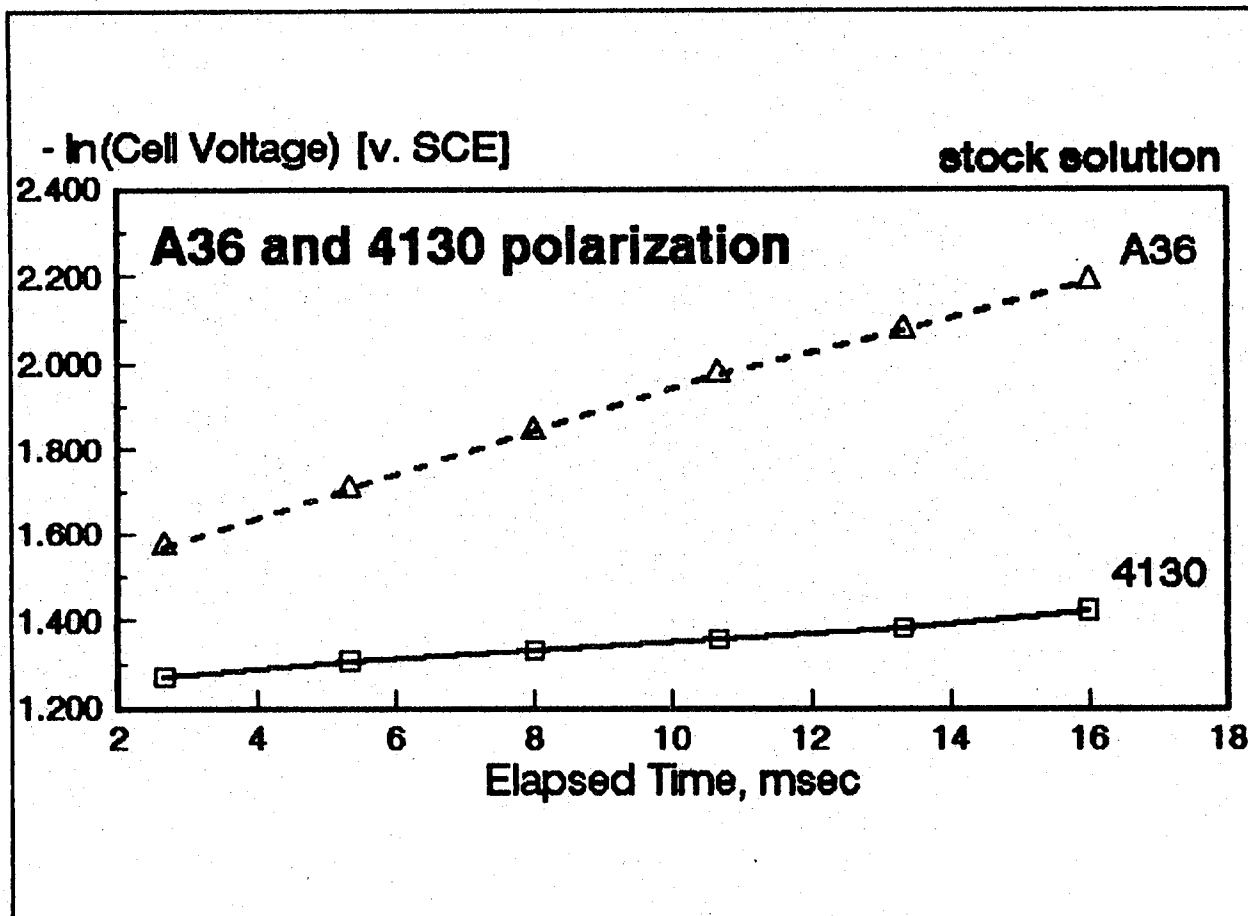


Figure 13 - A comparison of polarization kinetics for the A36 and 4130 alloy steels in the stock solution [0.1 KH_2PO_4 , pH 7]. Current amplitude was ± 2 mA, cycle reverse frequency was ± 20 mS.

In Figure 13 are compared polarization kinetics for our two reference materials, the A36 carbon steel and the 4130 low alloy steel. The operational variables were selected by trial and error to produce the optimum conditions for producing the greatest difference in behavior between the two - 20 mS current reversal frequency with a 2 mA current amplitude. What is interesting to note is that the A36 alloy evidences a larger degree of polarization than does the 4130 steel. Remember, now, the 4130 is more resistant to atmospheric corrosion than the A36. Furthermore, the IR drop [film electrical resistance] is substantially greater for the A36 material. Intuitively, you might think that this is contradictory in terms of the known corrosion resistance of the low alloy steel. It must be emphasized that corrosion resistance lies not necessarily with electrical resistivity, but with passivity - with the resistance

to ion transport through the barrier layer. The proof of the pudding, so to speak, will lie with ability of a barrier layer to retain its ionic resistivity in the presence of aggressive or corrosive chemical species. Whatever, we can say at this point that polarization behavior of the A36 alloy is distinguished by a larger electrical resistance which, in the presence of impressed anodic currents, results in larger [more positive] degrees of polarization - larger electrical fields or potential drops across the barrier corrosion product layer.

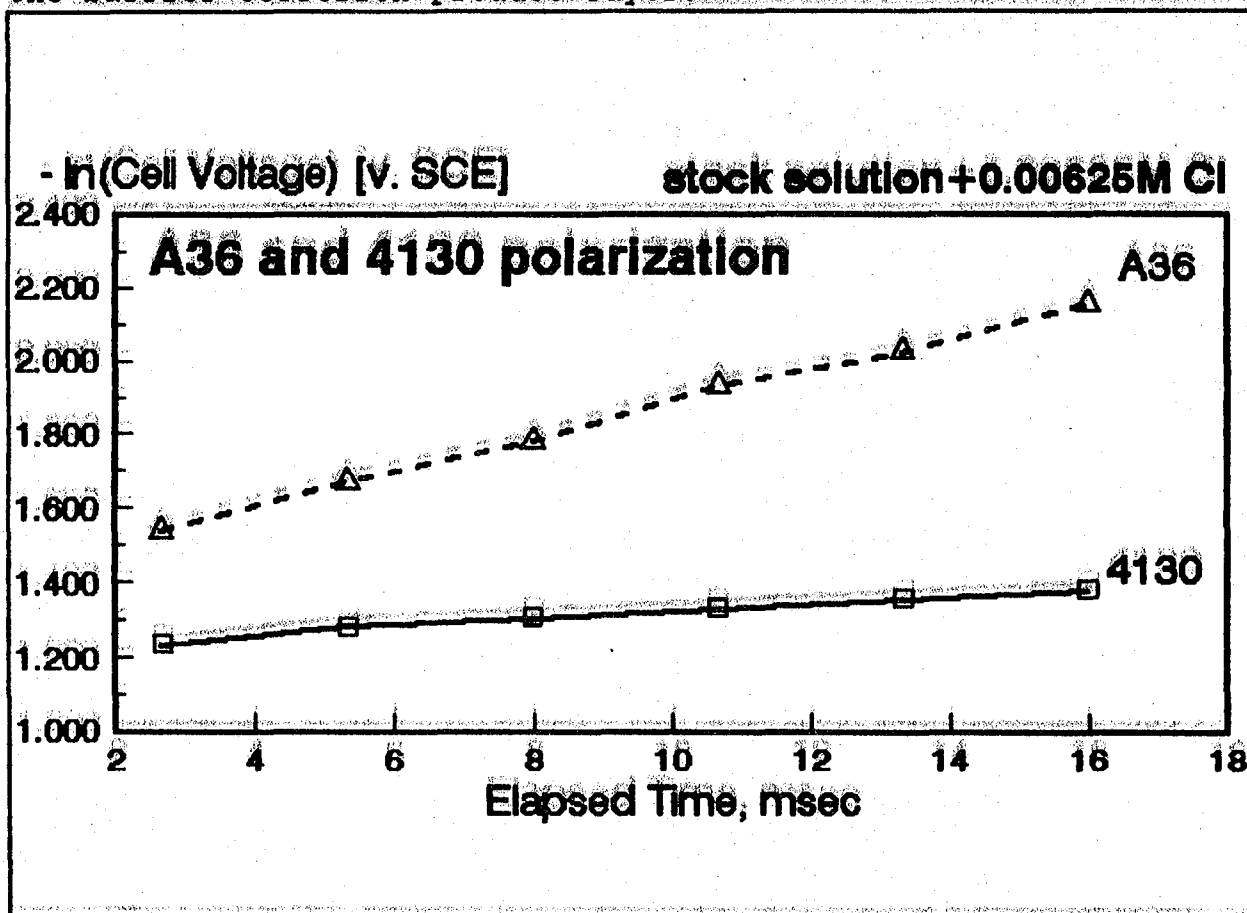


Figure 14 - A comparison of polarization kinetics for A36 and 4130 steels in the stock solution to which has been sufficient chloride ion to bring the overall Cl^- concentration to $6.25 \times 10^{-3} \text{ M}$.

Immediately upon addition of chloride ions, here producing a concentration in the stock solution of $6.25 \times 10^{-3} \text{ M}$, just above the minimum concentration required to produce pitting in low carbon steels, there are changes in polarization behavior between the two metals. These results are shown in Figure 14. There is little apparent difference between polarization kinetics for the two materials. However, there are differences in polarization degree.

In order to better visualize what the differences are, the

data contained in Figures 13 and 14 are compared by replotting and comparing the polarization behavior of each alloy with, and without, chloride ions being present.

Notice that there is little change in the kinetics of polarization, but a noticeable decrease in the IR drop across the film - the film has become more electrically conductive [Figure 15]. Similarly, when the behavior of the 4130 alloy is compared in stock and chloride containing solution, there is also a decrease in IR drop across the corrosion product, but the relative amount of the decrease is far less [Figure 16].

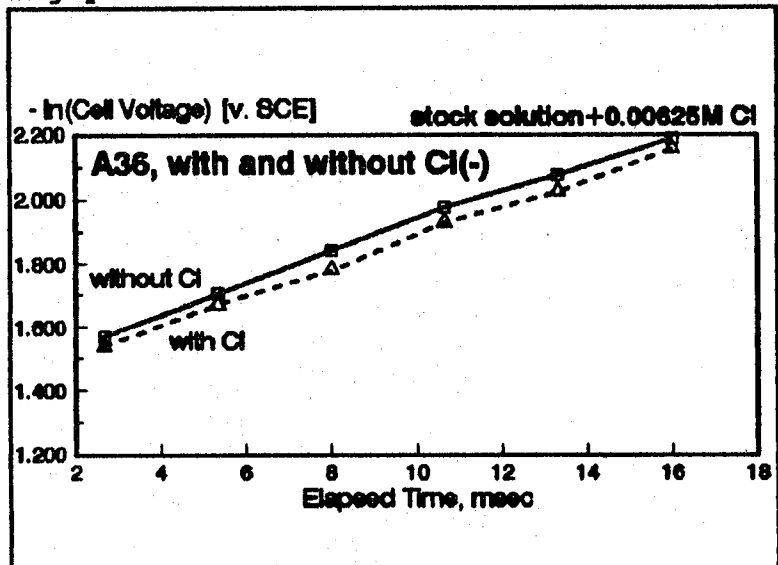


Figure 15 - A comparison of polarization behavior for A36 with, and without, chloride ions being present [from Figures 13 and 14].

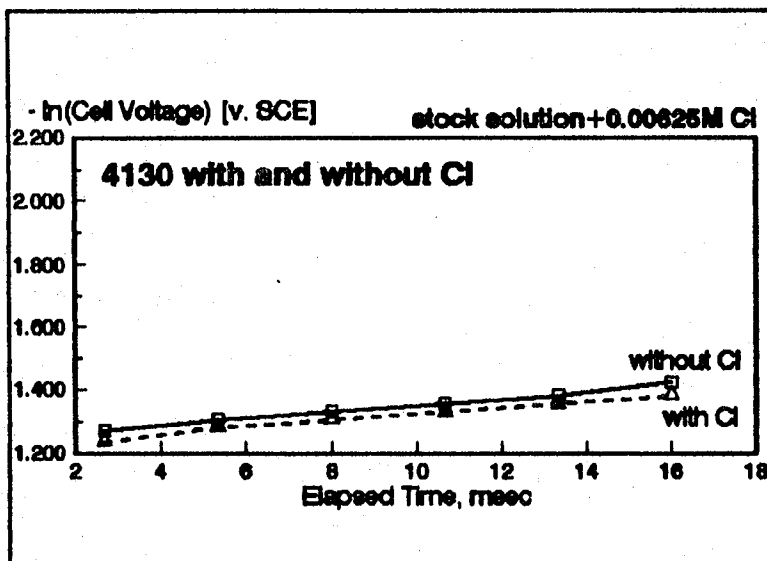


Figure 16 - Polarization behavior of 4130 with and without Cl^- .

There is little other than speculation as to the interpretation of this behavior. The fact that the degree of polarization is so much greater for the A36 alloy indicates that there is a greater driving force for migration of negatively charged anionic species into the film toward the metal/film interface. This, by itself, does not necessarily result in increased electronic conductance - unless, the chloride ion somehow leads to the

production of electronic charge carriers within the corrosion product. Perhaps, just perhaps, chloride ions within the corrosion product lead to an increased concentration of negative charge carriers, increasing the n-type extrinsic semiconductivity

of the barrier layer.

Whatever the explanation, within a few minutes, the IR drop decrease trend continues, until, after 5 minutes, the A36 has completely lost its capacity for producing an electrically resistive barrier layer completely [Figure 17].

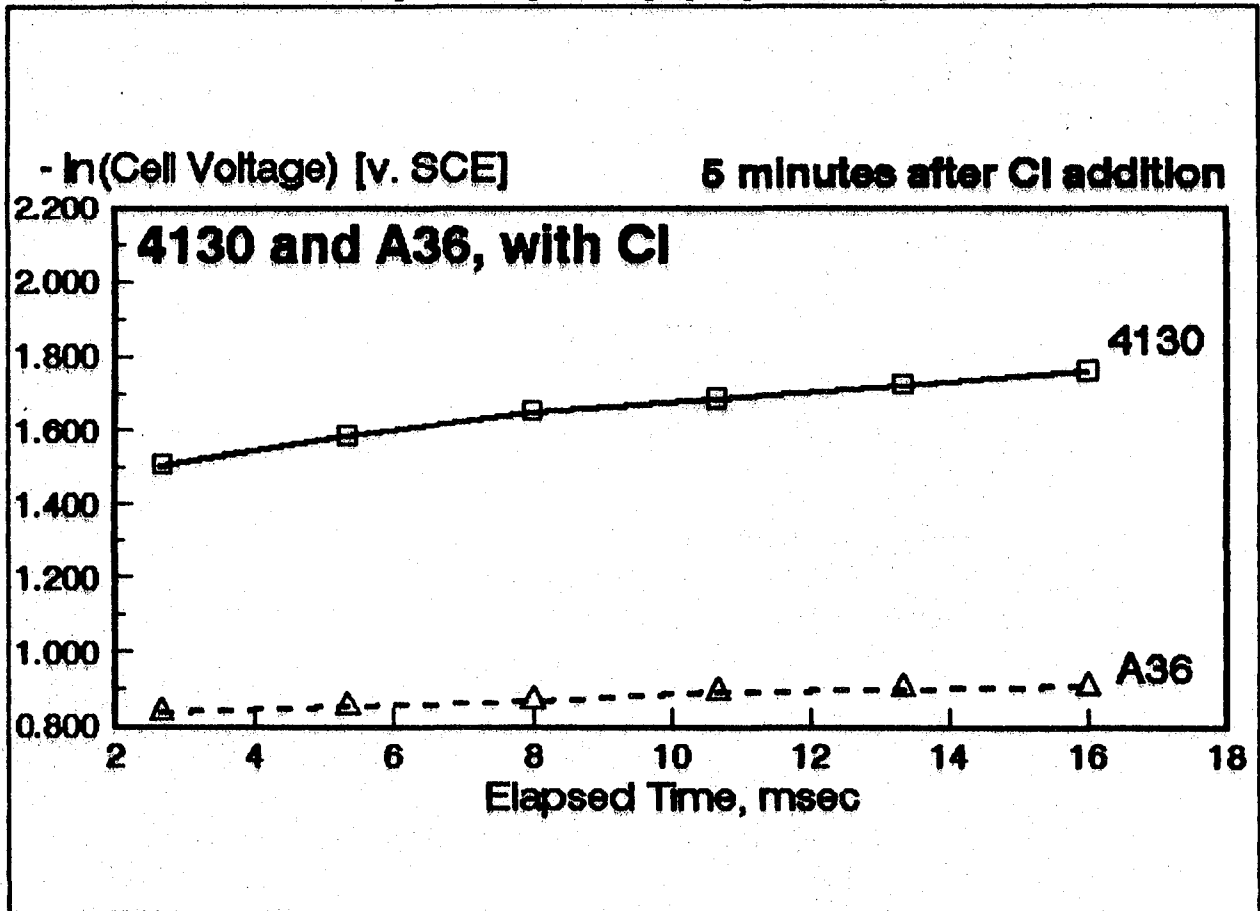


Figure 17 - After 5 minutes of RCRV in the presence of chloride ion, A36 has lost its capacity for production of electrically resistive corrosion products while 4130 is hardly affected at all.

Notice that the 4130 is hardly affected at all.

Bear in mind that this behavior has been measured without the occurrence of noticeable corrosion attack on the A36 alloy - only the tendency has been measured.

4.0 CONCLUSIONS

- a. Galvanostatic measurements represent a more natural approach to the modelling and development of accelerated test methods than do conventional potentiostatic methods.
- b. Periodic or cyclic current reversal tends to simulate concurrent anodic and cathodic reactions on a freely corroding metal surface better than do potentiostatic methods where anodic and cathodic processes occur on separate electrode surfaces.
- c. Development of highly resistive barrier layers which result in large degrees of polarization during anodic current cycles appear to be directly associated with susceptibility to atmospheric corrosion.
- d. Repetitive Current Reversal Voltammetry [RCRV] has been demonstrated to be a highly sensitive means with which to differentiate relative susceptibility to localized corrosion attack.

5.0 RECOMMENDATIONS FOR FUTURE WORK

- a. Experimentation must be continued with attention focussed on variations in polarization behavior as a function of solution composition. This would require modification to the existing electrochemical cell used in these studies.
- b. Development of a standard test solution and procedure to be applied to a larger list of candidate materials. Emphasis must be placed on establishing experimental methodology which is not limited by the experience or skill of the operator - "idiot proof".
- c. For scientific purposes, parallel studies of mechanistic implications of polarization kinetics should be accomplished. This will require "up-grading" of the equipment used - a digital oscilloscope with computer interfacing would speed up the data acquisition and interpretation process.
- d. The relationship between polarization behavior and both current amplitude and frequency needs to be established in more detail than has been done for these feasibility studies. It is possible that the results of these experiments may be integrated with experimentation using AC impedance techniques thus permitting more meaningful interpretation of alternating current methods than has been achieved to date.